

## ABSTRACT OF THE DISCLOSURE

Method is provided for selectively opening rings of polyhedral oligomeric silsesquioxane (POSS) compounds to form functionalized derivatives thereof or new POSS species. Per the inventive method, the POSS compound is reacted with an acid to selectively cleave bonds in the POSS rings to add functionalities thereto for grafting, polymerization or catalysis, to thus form new families of POSS derived compounds. Also provided are the new compounds so formed. Method is also provided for expanding rings of POSS compounds. Per the inventive method, a POSS compound is reacted with silane reagents to obtain an expanded POSS framework with added Si ring substituents to form new families of POSS compounds. Also provided are the new compounds so formed.